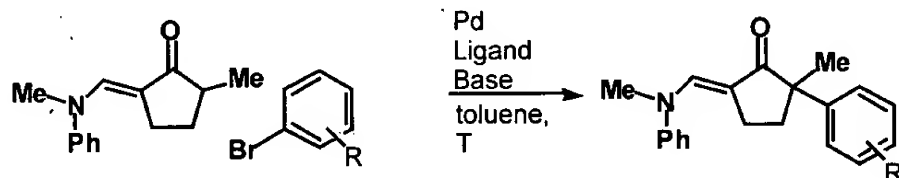


Figure 1

Examples of the Asymmetric Arylation of 2-Methylcyclopentanone Bearing a Blocking Group at the 5-Position

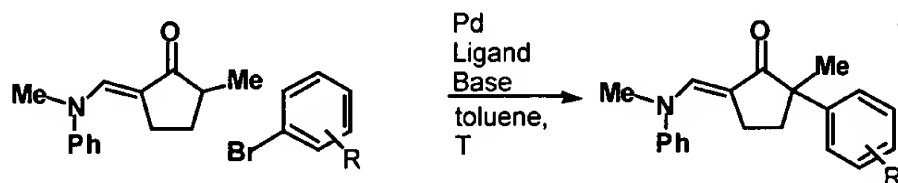


R	Ligand	%Pd	%L	Base	T C°	Y%	ee %
4- ^t Bu	(S)-BINAP	10	15	NaHMDS	100	67	90
4- ^t Bu	(S)-BINAP	10	15	NaO ^t Bu	100	70	89
4- ^t Bu	(R)-QUINAP	5	7.5	NaO ^t Bu	90	67	23
4- ^t Bu	(R)-MOP	10	15	KO ^t Bu	100	68	34
4- ^t Bu	(S)-BINAP	10	15	KO ^t Bu	100	54	84
4- ^t Bu	(R)-QUINAP	10	15	KO ^t Bu	100	23	15
4- ^t Bu	(S)-BINAP	10	15	KO ^t Bu	100	63	85
4- ^t Bu	(S)-BINAP	10	15	KHMDS	100	51	86
4- ^t Bu	(-)-1	5	7.5	NaO ^t Bu	rt	93	68
4- ^t Bu	(-)-1	5	7.5	NaO ^t Bu	rt	99	67
3-OMe	(S)-BINAP	10	15	NaO ^t Bu	100	91	85
4-OMe	(S)-BINAP	5	10	NaO ^t Bu	100	55	62
4-OMe	(S)-BINAP	10	15	NaO ^t Bu	100	65	57
3-(2-dioxolane)	(S)-BINAP	10	15	NaO ^t Bu	100	96	86

[1 = 2-(dicyclohexylphosphino)-2'-(dimethylamino)-1,1'-binaphthyl]

Figure 2

Additional Examples of the Asymmetric Arylation of 2-Methylcyclopentanone Bearing a Blocking Group at the 5-Position



5

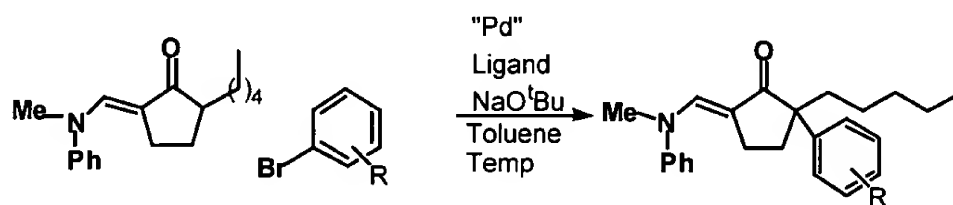
R	Ligand	%Pd	%L	Base	T C°	Y%	ee %
4-Me	(S)-BINAP	10	15	NaO ^t Bu	100	65	63
4-Me	(R)-QUINAP	10	15	NaO ^t Bu	100	82	25
4-Me	(-)-1	5	7.5	NaO ^t Bu	rt	88	75
2-Me	(S)-BINAP	5	10	NaO ^t Bu	100	52	10
2-Me	(S)-BINAP	5	10	NaO ^t Bu	100	48	8
3-Me	(S)-BINAP	5	10	NaO ^t Bu	100	70	80
3-Me	(S)-BINAP	5	10	NaO ^t Bu	100	72	80
4-CF ₃	(S)-BINAP	10	15	NaO ^t Bu	100	93	53
4-CF ₃	(S)-BINAP	10	15	NaO ^t Bu	80	80	44
4-CF ₃	(R)-QUINAP	5	7.5	NaO ^t Bu	90	54	43
3-CF ₃	(S)-BINAP	5	7.5	NaO ^t Bu	100	60	75
4-CN	(-)-1	5	7.5	NaO ^t Bu	rt	51	80

[1 = 2-(dicyclohexylphosphino)-2'-(dimethylamino)-1,1'-binaphthyl]

Figure 3

Asymmetric Arylation of 2-pentylcyclopentanone Bearing a Blocking Group at the 5-Position

5

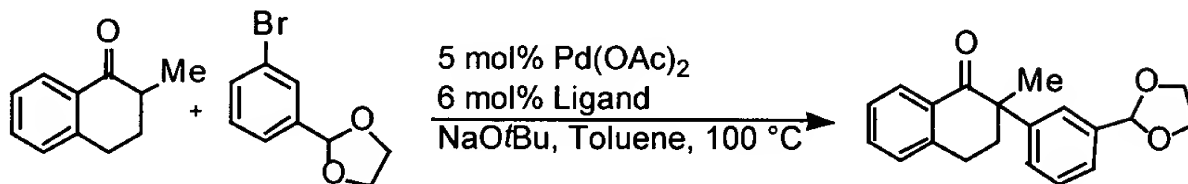


R	"Pd"	Ligand	%Pd	%L	T C°	Y%	ee %
H	Pd ₂ (dba) ₃	(S)-BINAP	10	15	93	84	93
H	Pd(OAc) ₂	(-)-1	10	15	72	78	72
3-Me	Pd(OAc) ₂	(S)-BINAP	10	15	100	70	99
4-CF ₃	Pd ₂ (dba) ₃	(S)-BINAP	10	15	100	71	90

10

[1 = 2-(dicyclohexylphosphino)-2'-(dimethylamino)-1,1'-binaphthyl]

Figure 4 α -Arylation of 2-Methyl-1-Tetralone--Ligand Effects



Ligand	Yield	ee
(S)-BINAP	69	84
(R)-QUINAP	43	84
(R)-MeO-BIPHEP	59	85
(S)-BIPHEMP	39	82
(R,R)-NORPHOS	38	40
(R)-MOP	19	8
(R)-PPF-OMe	38	1
(R)-(S)-JOSIPHOS	38	2
(S)-Et-DUPHOS ^a	8	12
(S)-Tol-BINAP ^b	26	30

(a) Reaction run with 10 mol% $\text{Pd}(\text{dba})_3$, 24 mol% (S)-Tol-BINAP, NaHMDS as base. (b) Reaction run with 2.5 mol% $\text{Pd}(\text{dba})_3$, 6 mol% (S)-Et-DUPHOS, NaHMDS as base.

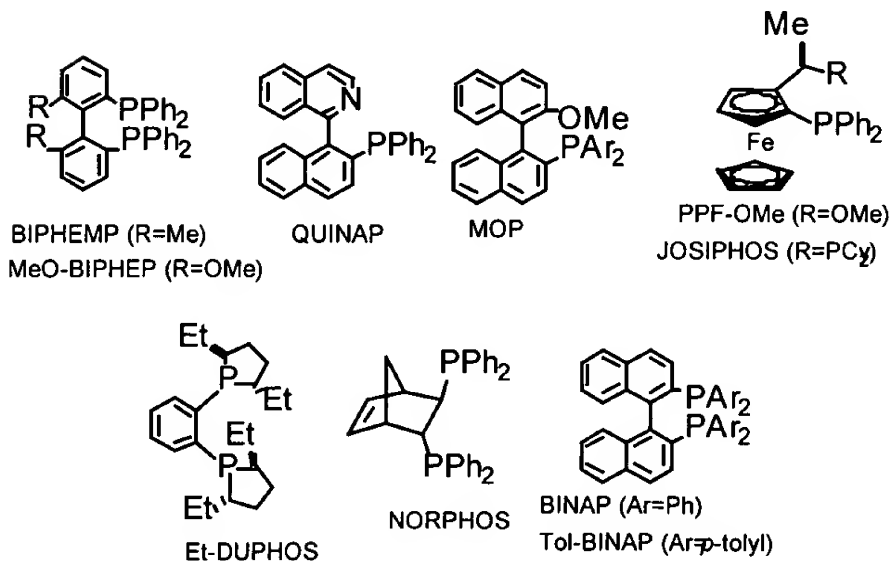


Figure 5. α -Arylations of Ketones in the Absence of a Phosphine Ligand.

$ \begin{array}{c} \text{R}-\text{C}(=\text{O})-\text{CH}_2-\text{R}' + \text{ArBr} \xrightarrow[\text{toluene, } 80^\circ\text{C}]{\text{Pd(OAc)}_2 \text{ or Pd}_2(\text{DBA})_3, \text{NaO}^t\text{Bu}} \text{R}-\text{C}(=\text{O})-\text{CH}(\text{Ar})-\text{R}' \end{array} $				
entry	Ketone	Aryl Bromide	Pd Source (mol %)	(% yield)
1			Pd ₂ (DBA) ₃ (1.5 mol %)	55%
2			Pd ₂ (DBA) ₃ (1.5 mol %)	54%
3			Pd(OAc) ₂ (1 mol %)	79%
4			Pd ₂ (DBA) ₃ (1.5 mol %)	46%
5			Pd ₂ (DBA) ₃ (1.5 mol %)	48%
6			Pd(OAc) ₂ (1 mol %)	71%
7			Pd(OAc) ₂ (1 mol %)	79%
8			Pd(OAc) ₂ (1 mol %)	83%
9			Pd ₂ (DBA) ₃ (0.5 mol %)	79%
10			Pd(OAc) ₂ (1.0 mol %)	64%